Synthesis and *X*-Ray Structure of a Cyclopenta[*d*]furo[2,3-*b*]furan Derivative from Isomerisation of 3,4,4-Triacetyl-2-methyl-*cis*-4,4a,5,7a-tetrahydrocyclopenta[*b*]pyran

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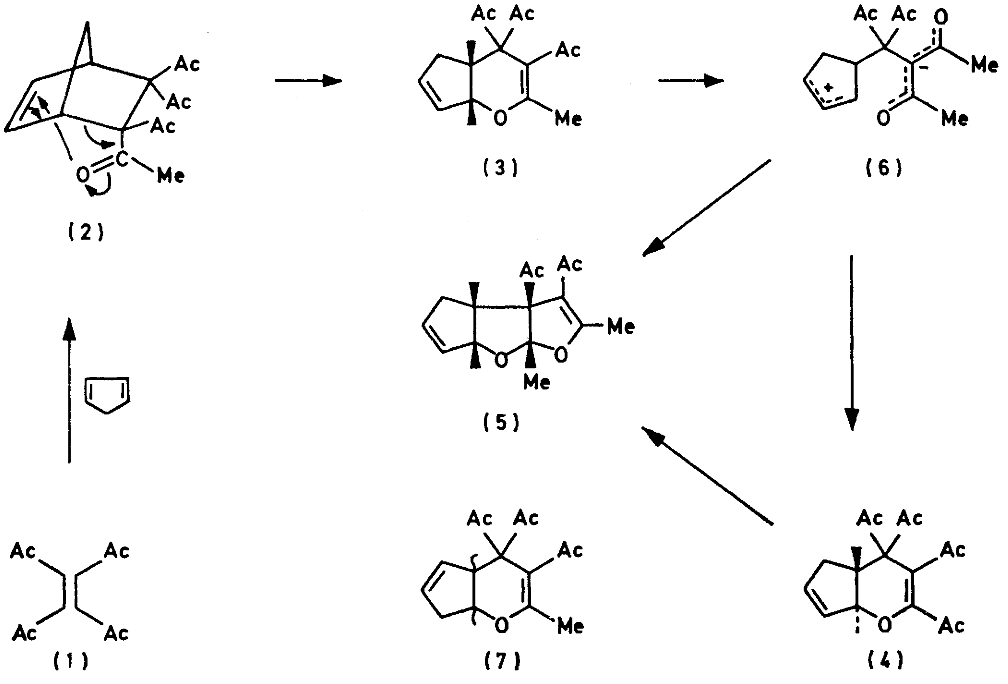
3,4,4-Triacetyl-2-methyl-*cis*-4,4a,5,7a-tetrahydrocyclopenta[*b*]pyran (3), obtained by reaction of tetra-acetylethylene (1) with cyclopentadiene, was converted into a mixture of the *trans*-isomer (4) and 3,3a-diacetyl-2,7a-dimethyl-3aα,4,6aα,7aα-tetrahydro-3bα*H*-cyclopenta[*d*]furo[2,3-*b*]furan (5), a new heterocyclic system, whose structure was definitively established by an *X*-ray analysis. Crystals are orthorhombic, a = 15.824(5), b = 15.465(5), c = 11.129(4) Å, Z = 8, space group *Pbca*. The structure was solved by direct methods and refined by least squares to a final R of 0.073 for 1 665 observed reflections. Some aspects of the mechanism are discussed.

As part of our investigation of the reactivity of 3,4-diacetylhex-3-ene-2,5-dione (tetra-acetylethylene) (1),[1-3] an highly activated unsaturated system, we recently reported[4] that a cyclopenta[*b*]pyran, namely 3,4,4-triacetyl-2-methyl-*cis*-4,4a,5,7a-tetrahydrocyclopenta[*b*]pyran (3), m.p. 75—76 °C, can be obtained by reaction of compound (1) with cyclopentadiene. Compound (3), whose structure was assigned on the basis of spectral evidence, mainly n.m.r., could result from a [3,3]-sigmatropic rearrangement of the Diels–Alder adduct (2).



SCHEME

Either after being set aside for a few months or on heating in glyme for 48 h, compound (3) changed into a tarry material from which we isolated an isomeric compound, m.p. 100—101 °C, whose identification rested on its spectroscopic properties and was formulated as 3,4,4-triacetyl-2-methyl-*trans*-4,4a,5,7a-tetrahydrocyclopenta[*b*]pyran (4).

In an effort to gain further insight into the extremely facile *cis–trans*-isomerisation of (3) into (4), which is unusual for a fused 5,6-ring system, we also found that the conversion of compound (3) was hastened by a brief heating above its melting point. T.l.c. of the melted material indicated it to consist almost exclusively of two compounds in the ratio 3 : 2 (based on the n.m.r. spectrum). The same mixture was obtained when a catalytic amount of hydrochloric acid was added to a methanolic solution of (3) at room temperature. A pure sample of each compound was obtained by careful preparative t.l.c. The faster running band, which accounted for *ca.* 60% of the reaction mixture, gave the cyclopenta[*b*]pyran (4), the slower band a colourless solid (5), m.p. 114—115 °C.

The u.v. absorption at 274 nm and the presence of a very strong band at *ca.* 1 600 cm^{-1} in the i.r. spectrum of

(5) were indicative of a conjugated –CO–C=C–O–system, as in isomers (3) and (4). The ^1H n.m.r. spectrum in deuterioacetone displayed four singlets (integral ratio 3 : 5 : 3 : 3) at δ 1.35, 2.04, 2.22, and 2.30 for the methyl groups (the signal at δ 2.04 masked almost completely a resonance, attributable to the methylene ring protons, which appears as a structured multiplet at *ca.* δ 2.11 in deuteriobenzene), two single-proton multiplets centred at δ 3.91 and 5.34 and a multiplet (2H) between δ 5.50 and 5.90. These signals were assigned to H-3b, H-6a, and olefinic protons respectively, on the basis of chemical shifts and spin-decoupling experiments. Irradiation at δ 3.91 did not change the pattern of the resonance at lowest field, whereas it reduced the doublet of multiplets ($J_{3b,6a}$ 7.5) at δ 5.34 (H-6a) to a sharp multiplet; the lack of any appreciable coupling between H-3b and the olefinic protons ruled out the double-bond isomers represented by structure (7). Irradiation at δ 5.34 (H-6a) caused the six-components pattern of H-3b to become a doublet of doublets ($J_{4',3b}$ 7.5; $J_{4'',3b}$ 2.7); such a remarkable difference for the coupling constants was in full agreement with the structure (5), whose Dreiding model exhibited different dihedral angles between H-3b and the methylene protons.

However only an *X*-ray analysis led us to establish for (5) the structure 3,3a-diacetyl-2,7a-dimethyl-3aα,4,6aα,-7aα-tetrahydro-3bα*H*-cyclopenta[*d*]furo[2,3-*b*]furan.

EXPERIMENTAL

I.r. spectra were measured for dispersions in potassium bromide with a Perkin-Elmer 457 spectrometer and u.v. spectra for solutions in methanol with a Cary 14 recording spectrophotometer. ^1H N.m.r. spectra were recorded with a Perkin-Elmer R 32; chemical shifts are in p.p.m. downfield from tetramethylsilane as internal reference and coupling constants in Hz. Silica gel plates (Merck F_{254}) were used for analytical and preparative t.l.c.

Isomerisation of 3,4,4-*Triacetyl*-2-*methyl*-cis-4,4a,5,7a-*tetrahydrocyclopenta*[b]*pyran* (3).—Compound (3) (0.5 g) in methanol with a drop of hydrochloric acid was stirred at room temperature until the isomerisation was complete (*ca.* 40 min). Removal of solvent *in vacuo* gave a solid which was resolved by preparative t.l.c. in diethyl ether–light petroleum (b.p. 75—120 °C) (1 : 1). The faster-running band gave the *trans*-isomer (4), the slower one compound (5), m.p. 114—115 °C, (from light petroleum. b.p. 75—120 °C) (Found: C, 68.89; H, 6.94; M.W., 263.3. $C_{15}H_{18}O_4$ requires C, 68.69; H, 6.92%; M.W., 262.3) i.r. $\nu_{max.}$ 3 050, 1 695, 1 600.).

Crystal Data.—$C_{15}H_{18}O_4$, $M = 262.28$, Orthorhombic, $a = 15.824(5)$, $b = 15.465(5)$, $c = 11.129(4)$ Å, $U = 2\,723.47$ Å^3, $D_c = 1.28$ g cm^{-3}, $Z = 8$, $F(000) = 140$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 0.74 cm^{-1}. Space group *Pbca* from systematic absences $hk0$ when $h \neq 2n$, $h0l$ when $l \neq 2n$, and $0kl$ when $k \neq 2n$.

Intensity Collection.—An irregular rod-shaped fragment of dimensions *ca.* 0.8 × 0.4 × 0.5 mm was mounted on a Philips automated diffractometer (graphite monochromator, Mo-K_α radiation). Cell constants and orientation matrix were determined by a least-squares fit of 23 strong reflections. The intensities of 3 320 reflections were measured within 2θ 56° with the ω—2θ scan technique at a scan speed of 0.04° s^{-1} and a scanwidth of 1.2° in ω. Background measurements were taken at each end of the scan range for half the time of the scan. The intensities of two reflections monitored periodically during data collection did not show any significant variation. 1 665 reflections with $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement. Standard deviations on intensities I were calculated according to the expression: $\sigma(I) = [P + B_1 + B_2 + (kI)^2]^{1/2}$, where P is the total peak count, B_1 and B_2 are the left and right background counts, and $k = 0.04$. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were not applied; a ψ scan on the $\bar{1}13$ reflection showed a maximum deviation of 3% in intensity.

Structure Solution and Refinement.—The structure was solved by direct methods with the use of MULTAN.[5] The *E* map, calculated with the set of phases which gave the highest figure-of-merit and lowest residual, yielded the positions of all non-hydrogen atoms. One cycle of least squares on the atomic parameters with isotropic temperature factors, followed by two cycles with anisotropic factors, reduced the disagreement index *R* to 0.10. A difference-Fourier synthesis calculated at this point showed the hydrogen atom positions, with the exception of those bound to C(9), which were probably disordered. Hydrogen atoms were introduced in the calculations in these positions without further refinement and were assigned a common temperature factor *B* of 4.0 Å^2. A final least-squares cycle on the positions and temperature factors of the non-hydrogen atoms gave a final *R* value of 0.073. The function minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$. Two different set of weights were used in the refinement, *i.e.* unit weights and statistical weights $w = 4F_o^2/\sigma^2(F_o^2)$. Unit weights gave a better error-of-fit and slightly smaller standard deviations on the parameters.

Scattering factors for non-hydrogen atoms were taken from ref. 6 and for hydrogen from ref. 7. All crystallographic calculations were performed with a version of the '*X*-Ray' program system [8] which includes MULTAN.

Final positional parameters for the atoms are listed in Table 1. Observed and calculated structure factors as well as final thermal parameters are listed in Supplementary Publication No. SUP 22430 (22 pp.).*

DISCUSSION

Description of the Structure.—The ORTEP [9] drawing (Figure) shows clearly the three fused five-membered rings in the *cis,syn,cis*-configuration which form the molecular structure of compound (5). Table 2 reports bond lengths and angles in the molecule, and Table 3 equations of best least-squares planes through the rings and the angles between them.

One of the most interesting features of the structure is the presence of the conjugated system O(1)–C(2)=C(3)–C(10)=O(12), which had been expected on the basis of the u.v. and i.r. spectra. The five atoms are essentially coplanar, with a maximum deviation of 0.017 Å for C(2) from the best least-squares plane through them. The deviations of C(11) and C(9) from this plane are 0.023 and 0.079 Å. In agreement with this picture the double bond C(2)–C(3) [1.337(6) Å] is

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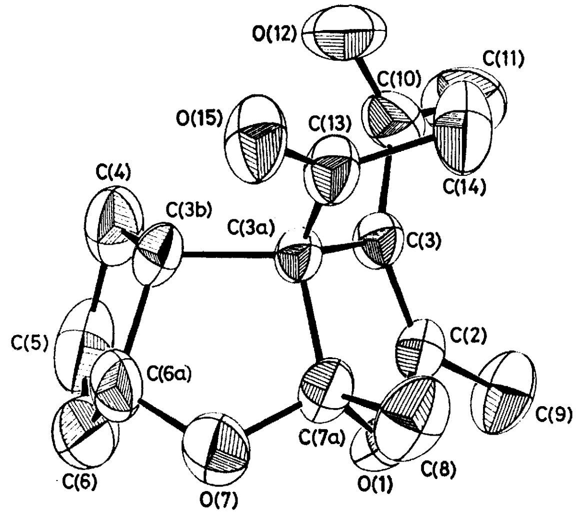
* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

longer than the analogous C(5)–C(6) bond [1.288(12) Å] and the single bond C(3)–C(10) [1.455(7) Å] is shorter than the analogous C(3a)–C(13) bond [1.531(7) Å]. The



ORTEP drawing of the molecule showing the atom labelling system used in the crystallographic analysis

coplanarity of the conjugated system causes steric hindrance between C(11) and C(9) [C(11)–C(9) 3.224(9) Å] which cannot be released by rotation around the C(3)–C(10) bond. As a consequence the angles C(2)–C(3)–C(10) and C(9)–C(2)–C(3) are respectively larger than C(3a)–C(3)–C(10) and O(1)–C(2)–C(9).

TABLE 1

Fractional atom co-ordinates (× 10^4), with estimated standard deviations in parentheses

(*a*) Non-hydrogen atoms

Atom	*x*	*y*	*z*
O(1)	3 087(2)	561(2)	4 203(3)
C(2)	3 794(3)	983(3)	4 499(4)
C(3)	4 018(3)	1 593(3)	3 708(4)
C(3a)	3 395(3)	1 598(3)	2 682(4)
C(3b)	3 694(3)	1 120(3)	1 515(4)
C(4)	4 596(3)	792(4)	1 470(5)
C(5)	4 519(5)	−143(5)	1 716(5)
C(6)	3 746(6)	−402(4)	1 718(7)
C(6a)	3 158(4)	304(4)	1 457(5)
O(7)	2 473(2)	405(3)	2 319(3)
C(7a)	2 684(3)	1 001(4)	3 188(4)
C(8)	1 879(3)	1 388(4)	3 683(5)
C(9)	4 162(4)	686(4)	5 679(4)
C(10)	4 744(4)	2 170(4)	3 682(5)
C(11)	5 417(4)	2 146(5)	4 633(6)
O(12)	4 825(3)	2 675(3)	2 843(4)
C(13)	3 029(3)	2 490(3)	2 392(4)
C(14)	2 957(5)	3 152(4)	3 379(5)
O(15)	2 778(3)	2 661(3)	1 387(3)

(*b*) Hydrogen atoms *

H(3b)	3 528	1 586	856
H(41)	4 899	872	676
H(42)	5 000	1 059	2 156
H(5)	5 145	−530	1 777
H(6)	3 745	−1 114	1 823
H(6a)	2 867	288	594
H(81)	1 588	1 664	3 067
H(82)	1 455	920	3 877
H(83)	2 097	1 844	4 437
H(111)	5 102	2 214	5 365
H(112)	5 486	1 522	5 091
H(113)	5 864	2 518	4 383
H(141)	2 923	2 880	4 123
H(142)	2 395	3 453	3 354
H(143)	3 198	3 661	3 103

* Estimated standard deviations are not reported because the positions of the hydrogen atoms were not refined.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses; those involving hydrogen atoms are not listed

(*a*) Bond distances

O(1)–C(2)	1.337(6)	C(13)–C(14)	1.507(8)
O(1)–C(7a)	1.465(6)	C(13)–C(15)	1.215(6)
C(2)–C(9)	1.508(7)	C(3b)–C(6a)	1.522(8)
C(2)–C(3)	1.337(6)	C(3b)–C(4)	1.515(7)
C(3)–C(10)	1.455(7)	C(4)–C(5)	1.476(10)
C(3)–C(3a)	1.509(6)	C(5)–C(6)	1.288(12)
C(10)–C(11)	1.502(8)	C(6)–C(6a)	1.464(10)
C(10)–O(12)	1.224(7)	C(6a)–O(7)	1.456(7)
C(3a)–C(7a)	1.561(7)	O(7)–C(7a)	1.377(6)
C(3a)–C(3b)	1.568(6)	C(7a)–C(8)	1.511(8)
C(3a)–C(13)	1.531(7)		

(*b*) Angles

C(7a)–O(1)–C(2)	109.1(4)	C(14)–C(13)–O(15)	119.9(5)
O(1)–C(2)–C(9)	112.8(4)	C(3a)–C(3b)–C(4)	118.0(4)
C(9)–C(2)–C(3)	133.3(5)	C(3a)–C(3b)–C(6a)	104.9(4)
O(1)–C(2)–C(3)	113.8(4)	C(6a)–C(3b)–C(4)	104.2(4)
C(2)–C(3)–C(3a)	109.2(4)	C(3b)–C(4)–C(5)	104.1(5)
C(2)–C(3)–C(10)	130.9(4)	C(4)–C(5)–C(6)	112.6(6)
C(3a)–C(3)–C(10)	119.8(4)	C(5)–C(6)–C(6a)	111.8(6)
C(3)–C(10)–C(11)	122.0(5)	C(6)–C(6a)–O(7)	115.0(5)
C(3)–C(10)–O(12)	119.3(5)	C(6)–C(6a)–C(3b)	104.8(5)
C(11)–C(10)–O(12)	118.6(5)	O(7)–C(6a)–C(3b)	107.3(4)
C(3)–C(3a)–C(3b)	115.3(4)	C(6a)–O(7)–C(7a)	110.8(4)
C(3)–C(3a)–C(7a)	101.2(3)	O(7)–C(7a)–C(3a)	108.4(4)
C(3)–C(3a)–C(13)	114.3(4)	O(7)–C(7a)–O(1)	109.7(4)
C(3b)–C(3a)–C(13)	111.4(4)	O(7)–C(7a)–C(8)	108.5(4)
C(3b)–C(3a)–C(7a)	103.8(4)	C(8)–C(7a)–C(3a)	120.3(5)
C(7a)–C(3a)–C(13)	109.6(4)	C(8)–C(7a)–O(1)	105.7(4)
C(3a)–C(13)–C(14)	119.2(4)	O(1)–C(7a)–C(3a)	103.8(3)
C(3a)–C(13)–O(15)	120.9(4)		

(*c*) Selected intramolecular distances <3.5 Å

C(2) ··· C(8)	3.225(7)	C(7a) ··· C(14)	3.362(8)
C(2) ··· C(11)	3.138(8)	C(7a) ··· O(15)	3.260(6)
C(3) ··· C(8)	3.400(7)	C(8) ··· C(13)	2.877(8)
C(3) ··· C(14)	2.961(8)	C(8) ··· C(14)	3.235(9)
C(3a) ··· O(12)	2.816(6)	C(9) ··· C(10)	3.325(8)
C(3b) ··· C(10)	3.349(7)	C(9) ··· C(11)	3.224(9)
C(3b) ··· O(12)	3.342(6)	C(10) ··· C(13)	3.109(8)
C(3b) ··· O(15)	2.793(6)	C(10) ··· C(14)	3.226(9)
C(4) ··· C(10)	3.265(8)	O(12) ··· C(13)	2.900(7)
C(4) ··· O(12)	3.309(8)	O(12) ··· C(14)	3.104(9)
O(7) ··· C(13)	3.342(7)		

(*d*) Intermolecular distances <3.5 Å

O(15) ··· C(2$^{\mathrm{I}}$)	3.376(6)	C(6a) ··· O(1$^{\mathrm{II}}$)	3.458(7)
O(15) ··· C(9$^{\mathrm{I}}$)	3.457(7)		

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

I $x, \frac{1}{2} - y, z - \frac{1}{2}$ II $\frac{1}{2} - x, -y, z - \frac{1}{2}$

Reaction Mechanism.—It must be pointed out that the conversion of compound (3) into (4) and (5) is quantitative. The course of the reaction was followed by recording the n.m.r. spectra of the mixture after various conversion periods, and we never detected any other compound.

The formation of the *trans*-isomer (4) may involve (Scheme) the pyran ring-opening of the *cis*-cyclopenta[*b*]pyran (3) followed by ring closure to a thermodynamically more stable isomer. A plausible intermediate in such a mechanism may be the dipolar species

Table 3

Equations of planes through the five-membered rings of (5) in the form $Ax + By + Cz - D = 0$. Deviations (Å) of atoms from the planes are given in square brackets. Acute angles between the normals to the planes are in degrees

	A	*B*	*C*	*D*
(*a*) Ring 1	−0.4747	0.7020	0.5309	0.8546
[O(1) −0.082, C(2) 0.021, C(3) 0.047, C(3a) −0.086, C(7a) 0.100]				
(*b*) Ring 2	9.8266	−8.6113	6.1392	3.6351
[C(3a) −0.028, C(3b) −0.039, C(6a) 0.100, O(7) −0.130, C(7a) 0.098]				
(*c*) Ring 3	−0.6941	1.8387	11.0393	1.5267
[C(3b) 0.095, C(4) −0.077, C(5) 0.028, C(6) 0.036, C(6a) −0.082]				

Angles (°) between planes:

(1)–(2) 66.8, (1)–(3) 50.5, (2)–(3) 63.4

(6) whose lifetime must be long enough to allow free conformational rotation.

In the case of acid-catalysed isomerisation it seems reasonable to suggest an analogous protonated intermediate which could arise by formal protonation of (3) on the pyran oxygen followed by ring-opening.

The same dipolar ion may rearrange in a different way to form two furan rings and give rise to isomer (5). Since its stereochemistry is *cis,syn,cis* the nucleophilic attack on the cyclopentene carbocation must be led by the oxygen of the acetyl group on the same part of H(4a) and H(7a).

A pseudo-concerted mechanism cannot be excluded for compound (5), but in this case also the C(6a)–O(7) bond must be formed by the acetyl group already mentioned, which can assume a suitable position in a boat-like conformation of the pyran ring. However, a stepwise mechanism seems more likely since the isomerisation of compound (3) may be acid-catalysed.

Thermal equilibration experiments on (4) and (5) were unsuccessful. On prolonged heating both compounds (4) and (5) decomposed completely to form many products, none of which (t.l.c.) were known isomers. Instead, when a methanolic solution of the *trans*-isomer (4) with a catalytic amount of hydrochloric acid was heated under reflux for 8 h, it rearranged to the thermodynamically more stable (5).

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